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SPIN-ORBIT COUPLING AND ENERGY SHIFTS IN SINGLE CRYSTAL AND PYROLYTIC GRAPHITE

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SPIN-ORBIT COUPLING AND ENERGY SHIFTS IN SINGLE

CRYSTAL AND PYROLYTIC GRAPHITE

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SUMMARY

A study of the spin-orbit coupling energy is made in both pure natural single crystals of graphite and in several highly ordered pressure annealed samples of pyrolytic graphite. This is done by observing splittings of Landau level crossings of the Fermi energy as the magnetic field is increased. Fields ranged to 10 teslas and temperatures were near 1.1 K. Quantities studied were the electrical magnetoresistance, the Hall effect, and the thermoelectric power. To interpret the data in terms of existing theories, shifts in the Fermi energy with magnetic field were studied. Experimental splittings are compared with a theory by McClure and Yafet and discrepancy is partially accounted for by large shifts in Fermi energy with magnetic field.

INTRODUCTION

Graphite is an important aerospace material because of its very high Young's modulus, and its extremely anisotropic and unusual properties (ref. 1). It has been formed into composite material for high strength applications, for example, reference 2. Graphite is a layered structure of carbon where the in-plane covalent bonding strength is as great as that for diamond. Highly perfected graphite (pyrolytic graphite, ref. 3) has only recently been synthesized, so it is not well studied or understood. The present report discusses one of many discoveries made in graphite while studying the very high magnetic field properties. These properties were found to be extremely anisotropic and thus potentially very useful in devices. More high field graphite work is reported in references 4 to 9.

The present report presents the first discovery and study of the effects of electron spin on the electronic structure of graphite in a strong magnetic field. It presents new evidence that pyrolytic graphite and perfect natural single crystals have much in common.

This report shows that the parameters needed to characterize other properties of pyrolytic and crystalline graphite will have to be modified to account for the spin effects reported herein.

In the presence of a very strong magnetic field, a conducting solid at low temperatures will have an electron distribution in momentum space characterized by Landau levels. Landau levels are cylinders with axes parallel to the magnetic field and contained within the zero field Fermi surface. Each cylinder corresponds to a discrete energy level for the electrons. Each Landau level is described by an orbital quantum number n and a spin quantum number having two values: one for spin up and one for spin down. In most materials the spin energy levels are degenerate. In graphite these levels are very slightly separated. There is a substantial spin angular momentum - orbital angular momentum coupling which causes "splitting" of the normally degenerate spin levels. The subject of this report is the study of the strength of the spin-orbit coupling. To do this properly requires a study of the energy shifts as a function of magnetic field. Fortunately both the spin splitting and Fermi energy shifts can be obtained from the same experimental data. This assures that the sample and experimental conditions are identical for both studies. Spin splittings are observed as double extrema in several transport coefficients as a function of field, and these are a measure of the conduction electron gfactors when shifts in the Fermi energy with field are accounted for.

Wagoner (ref. 10) observed conduction electron g-shifts from electron spin resonance studies. Spin resonance, however, measures the g-shifts averaged over the Fermi surface for particular magnetic field directions. Splittings of extrema in transport oscillations due to spin split Landau levels measure the spin-orbit splitting for particular magnetic field directions. Splittings of extrema in transport oscillations due to spin split Landau levels measure the spin-orbit splitting for particular points in the Brillouin zone (refs. 11 and 12). Knowing the location results from being able to identify a series of Landau level crossings of the Fermi energy $\mathbf{E_F}$ with a known location of the particular Fermi surface in the Brillouin zone (refs. 4 to 6, 9, and 13).

Figure 1 shows the Brillouin zone and Fermi surface of graphite. The Brillouin zone is hexagonal with the C-axis perpendicular to the hexagonal plane, as shown in figure 1. The Fermi surfaces are located along the vertical edges of the zone. Sections A are hole carriers and sections B are electrons (refs. 4 to 6, 9, and 13). McClure and Yafet (ref. 14) have calculated the g-shift for particular locations in the Brillouin zone. However, to compare with the spin resonance experiment, they had to take an average over the electron and hole Fermi surfaces in graphite for the magnetic field along the C-axis. This report presents results which can be compared directly with the McClure and Yafet theory, which in turn is based on the Slonczewski-Weiss (SW) band model (ref. 15).

EXPERIMENTAL RESULTS

The magnetoresistance is measured by a conventional four-probe technique and temperatures were regulated near 1.1 K by pumping on a liquid helium bath. For more details of this method see references 16 and 17.

Figure 2 shows the magnetoresistance of a natural single crystal as a function of magnetic field to 10 teslas (1 tesla = 10 kG) at 1.1 K for the magnetic field parallel to the [0001] axis (C-axis). Adams and Holstein (ref. 18) have shown that conductivity maxima occur at coincidence of Landau levels and $\mathbf{E_F}$. We experimentally find (refs. 4 to 6, and 9) that in graphite this implies resistivity minima at Landau level crossings of $\mathbf{E_F}$. References 6 and 9 show why this is true. Essentially it results from the Hall resistivity being much smaller than the magnetoresistance.

In figure 2 there are distinct minima at 6.60±0.02 and 7.40±0.02 teslas, where the n = 1 Landau level for electrons (in refs. 4, 5, and 13 it is shown that the electrons are located at B in fig. 1) crosses the Fermi energy. In highly ordered pressure annealed samples, we find resistivity minima less pronounced than for single crystals but occurring at nearly the same fields as for single crystals. An example of the pyrolytic data is shown in figure 3, where Hall resistivity ρ_{yx} and Hall conductivity σ_{xy} multiplied by H^2 are plotted, as well as the resistivity ρ_{yy} as a function of magnetic field at 1.1 K. The thermoelectric power as a function of magnetic field is shown in figure 4 for a temperature of 1.1 K. In pyrolytic samples we observe spin split maxima in the Hall conductivity (fig. 3) and minima in the thermoelectric power for the n = 1 electron level. The field values for extrema and splittings in resistance, Hall effect, and thermopower in natural single crystals as well as in several pyrolytic samples are listed in table I. In single crystals, figure 2 shows the spin split n = 1 hole Landau level resistivity minima appearing at 3.643±0.01 and 3.412±0.007 teslas. The spin split n = 2 electron level crossings appear at 2.936±0.005 and 2.992±0.007 teslas.

THEORY

The energy bands in zero field along the vertical edge of the hexagonal Brillouin zone edge are shown in figure 5. (See ref. 19 for a brief description.) The distance, in the $k_{\mathbf{x}}k_{\mathbf{v}}$ plane, from the vertical edge is σ . For nonzero σ , the energy eigenvalues are

$$E = \frac{1}{2} (E_1 + E_3) \pm \left[\frac{1}{4} (E_1 - E_3)^2 + \gamma_0^2 (1 - \nu)^2 \sigma^2 \right]^{1/2}$$
 (1)

$$E = \frac{1}{2} (E_1 + E_3) \pm \left[\frac{1}{4} (E_2 - E_3)^2 + \gamma_0^2 (1 + \nu)^2 \sigma^2 \right]^{1/2}$$
 (2)

which come from solutions of the effective mass Hamiltonian (refs. 15 and 19). (All symbols are defined in the appendix.) In equations (1) and (2)

$$\mathbf{E}_1 = \Delta + \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2 \tag{3}$$

$$E_2 = \Delta - \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2 \tag{4}$$

$$\mathbf{E}_3 = \frac{1}{2} \, \gamma_2 \Gamma^2 \tag{5}$$

and

$$\Gamma = 2 \cos \pi \xi \tag{6}$$

where ξ is the normalized distance along the vertical edge of the Brillouin zone shown in figure 1. In figure 5, $\sigma = 0$ and equations (1) and (2) reduce to E_1 , E_2 , and E_3 . In the preceding equations

$$\nu = \frac{\gamma_4 \Gamma}{\gamma_0} \tag{7}$$

The band parameters are

$$\gamma_0 = 3. \ 13 \ [2.85] \ eV$$

$$\gamma_1 = 0.4 \ [0.31] \ eV$$

$$\gamma_2 = -0.0183 \ [-0.0185] \ eV$$

$$\gamma_3 = +0.3 \ [0.29] \ eV$$

$$\gamma_4 = 0.25 \ [0.18] \ eV$$

$$\gamma_5 = -0.0183 \ eV$$

$$\Delta = 0.025 \ eV$$

$$a_0 = 2.456 \times 10^{-8} \ cm$$
(8)

which are determined by experiment. (See ref. 19, for example). The bracketed values in equation (8) and in equations which follow are from magnetoreflection data, unchecked against de Haas-van Alphen results (ref. 20).

The energy levels in a magnetic field were worked out by McClure (ref. 21) and Inoue (ref. 22), and the resultant secular equation is

$$\left(n + \frac{1}{2}\right)Q = \frac{E - E_3}{2} \left[\frac{E - E_1}{(1 - \nu)^2} + \frac{E - E_2}{(1 + \nu)^2}\right] \pm \left\{\frac{E - E_3}{2} \left[\frac{E - E_1}{(1 - \nu)^2} - \frac{E - E_2}{(1 + \nu)^2}\right]^2 + \frac{Q^2}{4}\right\}^{1/2} \tag{9}$$

and

$$Q = 3a_0^2 \gamma_0^2 \frac{eH}{2\hbar c} \tag{10}$$

Constants e, \hbar , c have their usual meaning, and H is the magnetic field. Equation (9) thus relates the energy E to the magnetic field strength H for particular ν values determined by equations (6) and (7).

The energy levels in a magnetic field can be found approximately by (e.g., ref. 11)

$$E_{\pm} = \left(n + \gamma \pm g \frac{m^*}{4m_o}\right) \frac{e\hbar H}{m^*c}$$
 (11)

where (ref. 22)

$$\gamma = \frac{1}{2} - \left\{ 2(2n+1) \left[1 - \left(\frac{E_3 - E_1}{E_3 - E_2} \right) \left(\frac{1+\nu}{1-\nu} \right)^2 \right] \right\}^{-1}$$
 (12)

so

$$g = \frac{2m_{O}c}{e\hbar} \left(\frac{E_{+}}{H_{+}} - \frac{E_{-}}{H_{-}}\right)$$
 (13)

This equation is used experimentally to obtain the g-factor.

McClure and Yafet (ref. 14) have worked out g-factors and shifts δg from the free electron value of 2.002, due to spin-orbit coupling. They get (after correction for a minus sign)

$$\delta g_{\pm} = -\frac{3\lambda a^2 \gamma_0^2 m_0 \left[2\Delta + 8\nu \gamma_1 \cos^2 \pi \xi + 4(\gamma_5 - \gamma_2) \cos^2 \pi \xi \right]}{4\hbar^2 \left| E_3 - E_F \right| D_+ \gamma_1 \cos \pi \xi}$$
(14)

where

$$D_{+} = \frac{2E_{F} - (E_{2} + E_{3})}{(1 + \nu \cos \pi \xi)^{2}}$$
 (15)

$$D_{-} = \frac{2E_{F} - (E_{1} + E_{3})}{(1 - \nu \cos \pi \xi)^{2}}$$
 (16)

where ν is given in equation (7) and the plus signs are for electron carriers. Parameter λ is the spin-orbit coupling constant and is a measure of the strength of the spin-orbit interaction. Other parameters and constants are the same as discussed earlier. Parameter γ_3 does not appear in any of the preceding equations because it was neglected in these derivations to simplify the analysis. Equation (8) shows that the magnitude of γ_3 is large compared to several other constants. Since these parameters enter the elements of the Hamiltonian linearly (ref. 23), this is a serious neglect.

Interpretation and Analysis of Experimental Results

In figure 2 the resistance minima determine the magnetic field values for crossings of E_F and the Landau levels. (This is discussed in detail in refs. 4 to 6, and 9). Using the experimental minima from figure 2, equation (9) is solved for E by computer. The resultant E values are then adjusted (by subtracting $2\gamma_2$) such that they become Fermi energy values. These numbers for electron carriers are

$$E = +0.0230 [0.0231] eV n = 1 (17)$$

$$E = +0.0169 [0.0170] eV n = 2$$
 (18)

$$E = +0.0156[0.0158] eV$$
 $n = 3$ (19)

(The bracketed values are from ref. 19.) Using a similar analysis for the hole carriers gives

$$E = 0.0164 \text{ eV} \qquad n = 1$$
 (20)

In figure 6 the energy values from equations (17) to (20) are plotted as a function of the magnetic field associated with the $n=1,\,2,\,3$ Landau level crossings. The mean value of magnetic field is taken for the n=1 levels where the splitting is large. For the n=1 electron spin split Landau level crossing, the values of E_+ and E_- are found from the graph. The field values for crossing the Fermi energy for spin+ and spin-are known from figure 2 (for the natural single crystal) and listed in table I. The curve in figure 5 thus gives

$$E_{\pm}(6.60 \text{ T}) = 0.0222 \pm 0.0002 \text{ eV}$$
 (21)

$$E_{(7.40 T)} = 0.0237 \pm 0.0002 \text{ eV}$$
 (22)

for the n = 1 electron Landau level. From equation (13) this gives

$$g = 2.7 \pm 0.4$$
 (23)

so

$$\delta g = 0.7 \pm 0.4$$
 $n = 1$ electron (24)

For the n=2 electron level E_{+} and E_{-} are approximately 0.0170 ± 0.0003 eV and equation (13) gives a g such that

$$\delta g = -0.0 \pm 0.3$$
 $n = 2$ electron (25)

For the n = 1 hole level, E is 0.0164 and equation (13) gives a g such that

$$\delta g = 3.0 \pm 0.5$$
 $n = 1 \text{ hole}$ (26)

However, if the Fermi level shift is accounted for as shown in figure 5, then

$$E_{+} = 0.0164 \text{ eV}$$
 (27)

and

$$E_{-} = 0.0168 \text{ eV}$$
 (28)

$$\delta g = +1.4 \tag{29}$$

McClure and Yafet analyzed Wagoner's data (ref. 10) using equation (14) and obtained

$$\lambda \simeq 3 \times 10^{-4} \text{ eV} \tag{30}$$

However, γ_3 was assumed to be zero, Fermi energy shifts with magnetic field were not considered, and a possible numerical error exists (J. W. McClure: private communication). Dresselhaus and Dresselhaus (ref. 24) have calculated the spin-orbit interaction in graphite, avoiding some of the simplifying assumptions made by McClure and Yafet, and find that λ should be on the order of 10^{-2} eV. Using McClure and Yafet's theory and the experimental g-values, we get

$$\lambda = -1.4 \pm 0.8 \times 10^{-3} \text{ eV} \quad n = 1 \text{ electron}$$
 (31)

$$\lambda = 1.4 \pm 4 \times 10^{-4} \text{ eV} \quad n = 2 \text{ electron}$$
 (32)

$$\lambda = 2.3 \pm 0.2 \times 10^{-3} \text{ eV} \quad n = 1 \text{ hole}$$
 (33)

These equations indicate that the magnitude of λ is on the order of 10^{-3} eV, which is an order of magnitude greater than McClure and Yafet's value but is smaller than found in reference 24. The values found in equations (31) to (33) do not agree with each other. The solution to this problem is discussed in the next section.

DISCUSSION AND CONCLUSIONS

Thus, in this report, a study of the spin-orbit coupling energy is made in both pure natural single crystals of graphite and in several highly ordered pressure annealed samples of pyrolytic graphite. This is done by observing splittings of Landau level crossings of the Fermi energy as the magnetic field is increased. Fields ranged to 10 teslas and temperatures were near 1.1 K. Quantities studied were the electrical magnetoresistance, the Hall effect, and the thermoelectric power. To interpret the data in terms of existing theories, shifts in the Fermi energy with magnetic field were studied.

In order to find the experimental g-shift using equation (13), the Fermi energy at spin-up and spin-down Landau level crossings has to be found from equation (9). Equation (9) is based on the SW band model and depends on the parameters of equation (8),

which need to be better determined. Equation (9) also neglects γ_3 , which may significantly affect the numbers found in equations (17) to (20) and thus the experimental gvalue. This is probably the cause of the sign discrepancy with the n=1 electron gvalue.

Equation (14) for the theoretical g-shift also neglects γ_3 , makes other simplifying assumptions, and depends on accurate values for the constants of equation (8). Thus there is a need for a determination of the best band parameter constants consistent with all available graphite data. There is also a need for more theoretical work to predict the relation between g-shifts and spin-orbit coupling energy in graphite, in order to better compare experiment with theory.

McClure (private communication) has recently pursued this theoretical work, including effects of γ_3 and Fermi level shifts, and gets approximate agreement between theory and experiment. The results depend critically on the parameters of equation (8).

J. Furdyna (private communication) has observed the effects of spin splitting of the n = 1 electron level on helicon propagation in a sample of pyrolytic graphite. The splitting appears roughly at the fields discussed in this report, for the n = 1 electron level.

Lewis Research Center,

National Aeronautics and Space Administration, Cleveland, Ohio, December 4, 1970, 129-02.

APPENDIX - SYMBOLS

Α	locations of holes in Brillouin zone					
a, a _o	graphite lattice parameter					
В	locations of electrons in Brillouin zone					
c	velocity of light					
D_+, D	parameters in McClure, Yafet theory					
E	energy					
$\mathbf{E}_{\mathbf{F}}$	Fermi energy					
\mathtt{E}_{\pm}	energy relative to band edge for spin up and spin down					
$\mathbf{E_1}, \mathbf{E_2}, \mathbf{E_3}$	parameters in Slonczewski-Weiss (SW) band model					
e	electric charge					
g	spin splitting factor					
$\delta {f g}$	spin splitting factor shift from 2.002					
Н	magnetic field strength					
$\mathrm{H}_{+},\mathrm{H}_{-}$	field values for spin up and spin down					
ħ	Plancks constant divided by 2π					
m*	effective mass					
m, n	integers					
^m o	mass of free electron					
Q	parameter in SW band model in a magnetic field					
lpha	field dependent parameter					
γ	phase factor					
$\begin{matrix} \gamma_0,\gamma_1,\gamma_2,\gamma_3,\\ \gamma_4,\gamma_5,\Delta \end{matrix}$	constants of SW band model					
Г	parameter in SW band model					
u	parameter in SW band model					
ξ	dimension along vertical edge of Brillouin zone					
σ	distance from vertical edge of Brillouin zone in $k_x k_y$ plane					
λ	spin-orbit splitting constant					

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TABLE I. - FIELD VALUES FOR SPIN SPLIT LANDAU LEVELS

Sample	Landau level	Magnetic field values, T ^a			
		Magneto- resistance	Hall coefficient	Thermopower	
Natural single	n = 1 electron	7.40±0.02 6.60±0.02			
crystal	n = 2 electron	2.992±0.007 2.936±0.005			
	n = 1 hole	3.643±0.01 3.412±0.007			
Pyrolytic graphite: b					
PG 5	n = 1 electron	7.54±0.05 6.92±0.1	7.56±0.05 6.93±0.1		
PG 4	n = 1 electron	7.54±0.05 6.92±0.1	7.53±0.05 6.82±0.1	7. 68±0. 05 6. 92±0. 1	
PG 3	n = 1 electron	7, 23±0, 2 6, 43±0, 2	7.45±0.1 6.80±0.1		

 $^{^{}a}$ 1 T = 10 kG.

^bPG 5, PG 4, and PG 3 refer to different samples of highly ordered pressure annealed pyrolytic graphite.

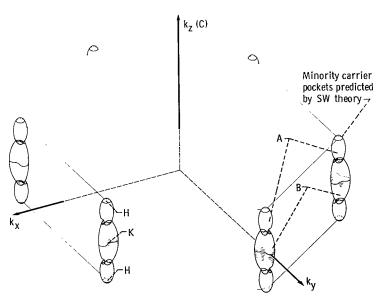


Figure 1. - Brillouin zone and Fermi surfaces of graphite. C-axis direction is marked. Section A are holes; section B are electrons; H and K are points along the Brillouin zone edge. (From ref. 19.)

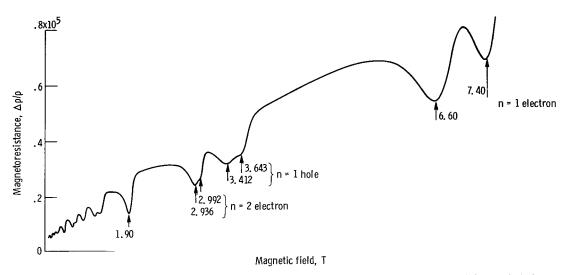


Figure 2. - Magnetoresistance as function of magnetic field at $1.1\,\mathrm{K}$. Field values at spin split minima are in teslas (1 T = $10\,\mathrm{kG}$). Natural single crystal graphite.

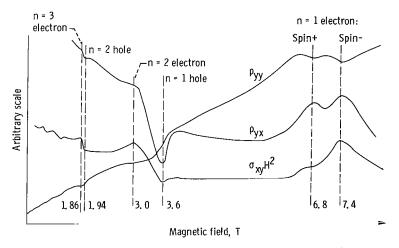


Figure 3. – Magnetoresistance ρ_{yy} , Hall resistivity, and Hall conductivity σ_{xy} times H^2 , as function of magnetic field at 1, 1 K. Spin splitting of n = 1 electron levels are marked.

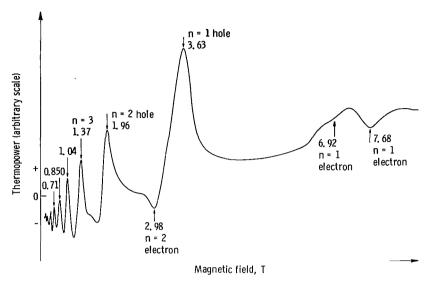


Figure 4. – Thermoelectric power as function of magnetic field at 1, 1 K. Spin splitting of n = 1 electron level is shown.

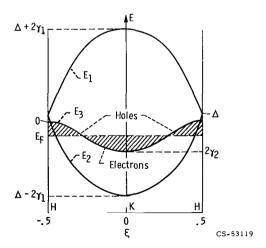


Figure 5. - Energy along vertical edge HKH (see fig. 1) of Brillouin zone (eqs. (1) to (5)). (From ref. 19.)

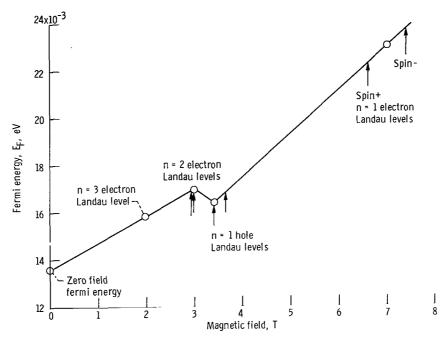


Figure 6. - Fermi energy as function of magnetic field, as obtained from experimental data of figure 2 and equation (9).